

Highly Ordered Hierarchical Anodes for Extreme Fast-Charging Batteries

Principal Investigator: Neil P. Dasgupta
University of Michigan, Ann Arbor

Annual Merit Review
DOE Vehicle Technologies Program
June 10-13, 2019

bat394

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Project start date: July 1, 2018
- Project end date: August 31, 2020
- Percent complete: 46%

Budget

- Total project funding: 1,667k
 - DOE share: 90%
 - Contractor share: 10%
- Funding for FY 2018: 883k
- Funding for FY 2019: 784k

Barriers

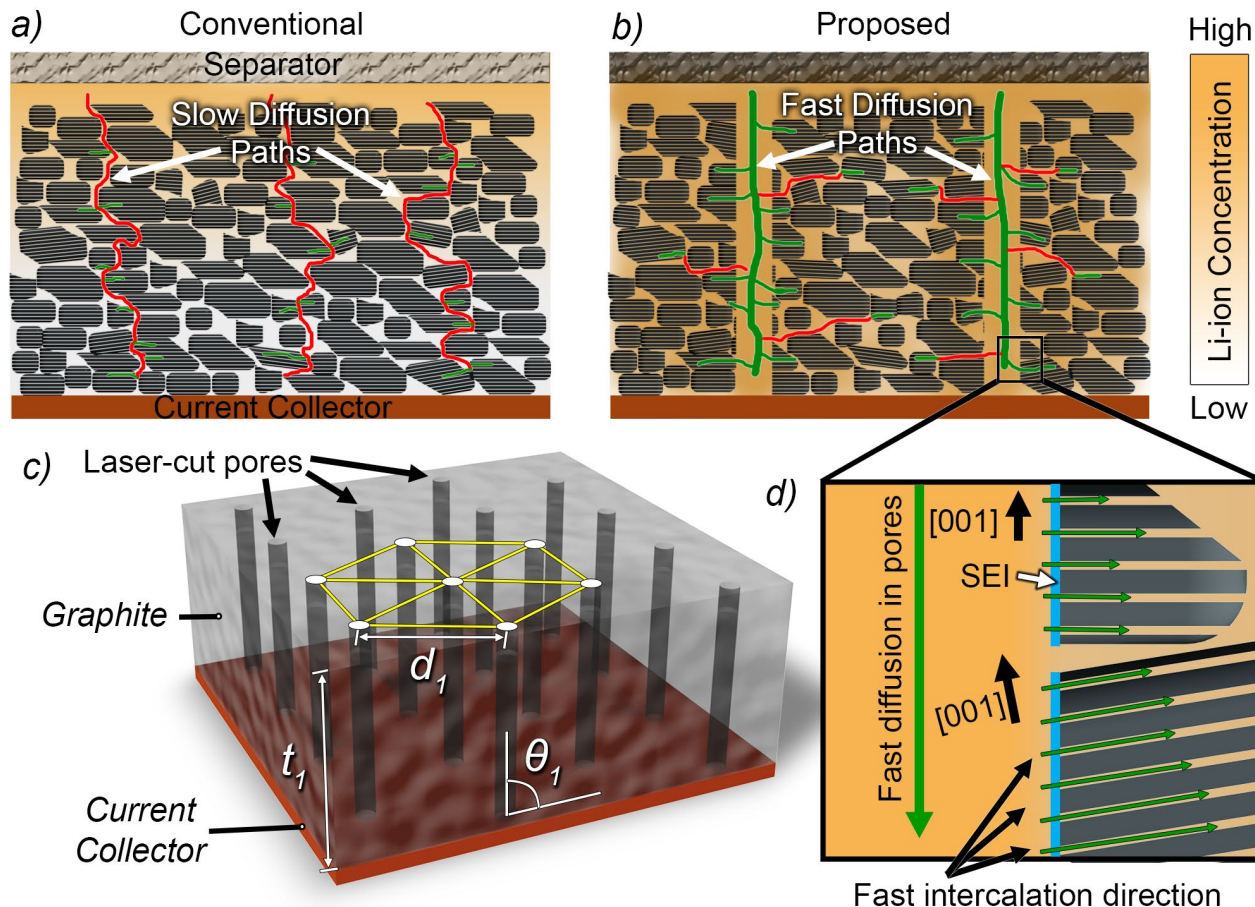
- Barriers addressed
 - Extreme fast charging of batteries with energy density ≥ 180 Wh/kg
 - Cycle life and durability of cells
 - 3-D electrode design

Partners

- Principal Investigators
 - Neil Dasgupta, Jeff Sakamoto, Katsuyo Thornton, Jyoti Mazumder (U-M)
 - Mohan Karulkar (Sandia National Lab)
- Collaborators
 - Andrew Jensen, Venkat Srinivasan (ANL)
 - Kandler Smith (NREL)
 - Mike Toney (SLAC)
 - Vanessa Wood (ETH Zürich)

Objectives and Relevance

Objective: Demonstrate >2 Ah pouch cells with an energy density ≥ 180 Wh/kg, capable of a 10-minute fast charge protocol, and 500 cycles with <20% fade in specific energy



Objectives and Relevance

Relevance:

- Overcome tradeoff between energy density and power density
- Demonstrate a scalable pathway for electrode modification that is directly compatible with existing roll-to-roll manufacturing
- Experimentally-informed modeling of electrolyte concentration gradients to optimize 3-D electrode architectures
- Improved fundamental understanding of Li plating through advanced metrology and *operando* characterization

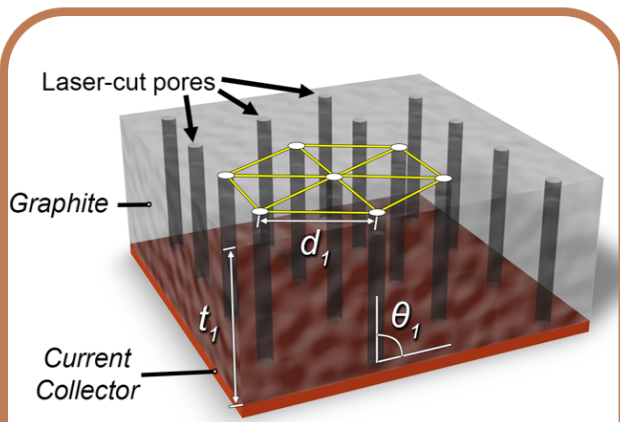
Impact:

- Enable 6C charging without significantly impacting energy density or manufacturing cost
- Accelerate public acceptance of EVs by reducing range anxiety and making re-charging competitive with refueling of IC engines

Milestones

Type	MS #	Milestone description	Milestone Verification	Quarter
MS	1.1	Demonstrate ability to create HOH anodes with pore diameter ranging from 20-50 μm and spacing between 100-200 μm	SEM data	Q1
MS	2.1	Simulate a charge/discharge cycle for a HOH half-cell with a fixed hole diameter and spacing at 1C, 4C and 6C and predict the concentration gradients as a function of C-rate.	Modeling data	Q2
MS	1.2	Demonstrate ALD LTO coatings on HOH anode surface with thickness ranging from 1-20 nm; cycle at C-rates from 1-6	XPS, SEM, cycling data	Q3
MS	3.1	Generate <i>operando</i> video microscopy data for HOH anodes for current densities ranging from 1-10 mA/cm^2	Video data	Q4
GN	G1	Demonstrate 200% improvement in capacity retention over 100 cycles at 4C rate and 100% improvement in capacity retention over 100 cycles at 6C rate	Cycling data	Q4
D	D1	Deliver 9 cells of $\geq 2\text{Ah}$ capacity with HOH anodes	DIC data	Q4
MS	1.3	Demonstrate ALD fast ion conductor on HOH anode with thickness ranging from 1-20 nm; cycle at C-rates from 1-6	TEM data	Q5
MS	2.2	Simulate a charge/discharge cycle for a HOH graphite half-cell at 1C, 4C and 6C and predict the concentration gradients as a function of hole diameter and spacing. Determine the optimal hole diameter and spacing.	Modeling data	Q6
MS	3.2	Use HPC and Rapid EIS to generate early Li plating markers in cycling efficiency, voltage, dQ/dV , and impedance during XFC; use markers to compare HOH/ALD treated cells and recommend optimal conditions to reach 80% capacity retention at 500 cycles.	EIS/HPC data	Q7
MS	3.3	Confocal Raman scans of HOH anodes for current densities ranging from 1-10 mA/cm^2	Raman data	Q8
D	D2	Deliver 18 cells, $\geq 2\text{Ah}$ capacity with improved HOH anodes	DIC data	Q8

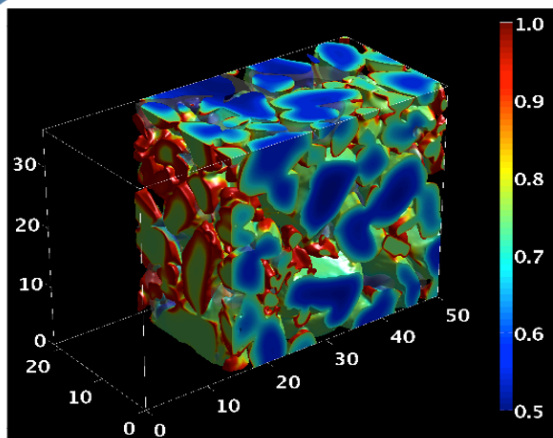
Approach



Design and Manufacturing

PIs: Dasgupta, Sakamoto, Mazumder, Thompson

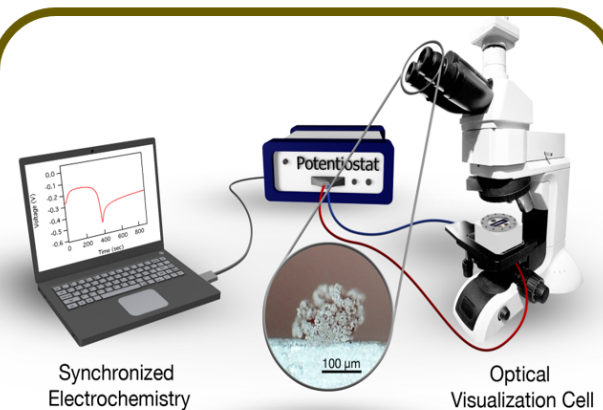
1. Design of HOH architecture
2. Laser manufacturing
3. Interface modification (ALD)
4. Scale up and automation of cell manufacturing



Computational modeling

PI: Thornton

1. Effect of porosity and tortuosity on transport
2. Hierarchical geometry
3. Electrolyte concentration and temperature dependence



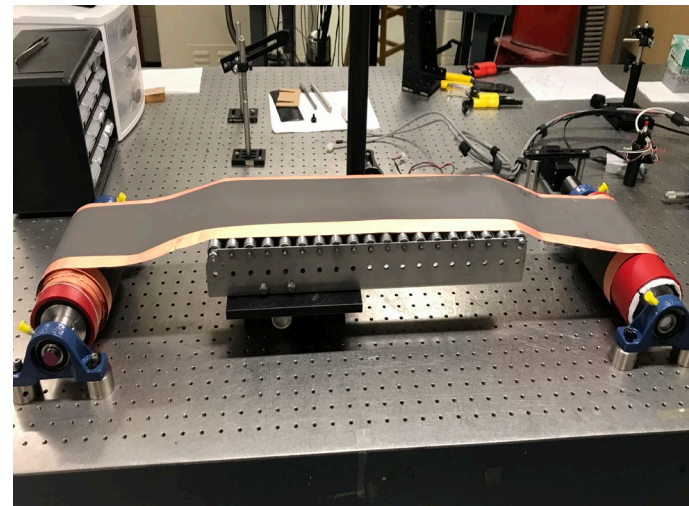
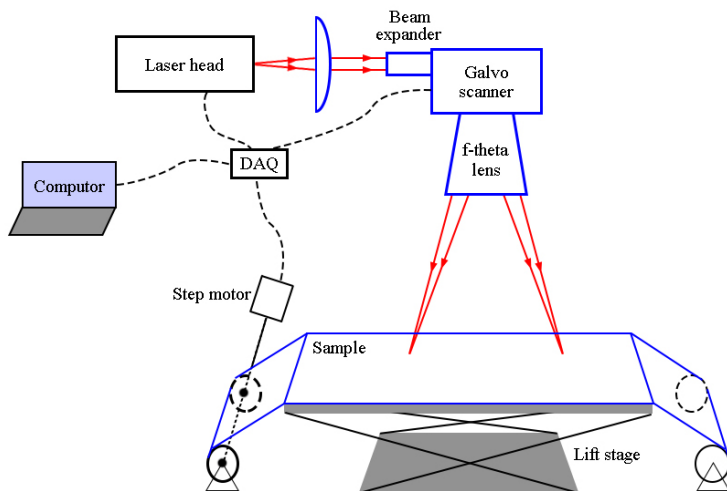
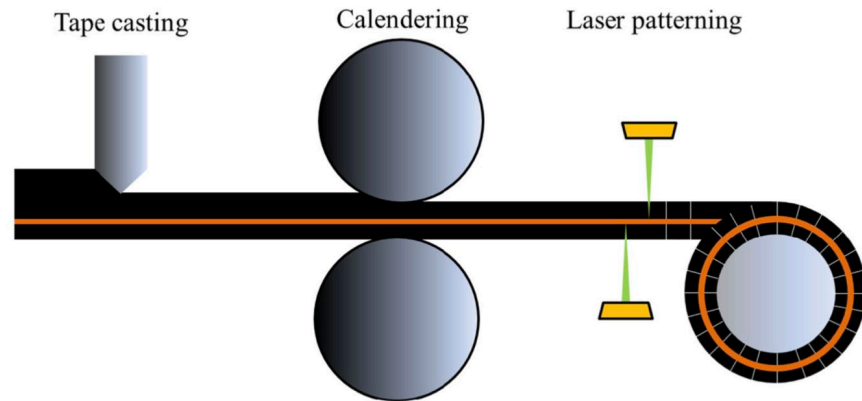
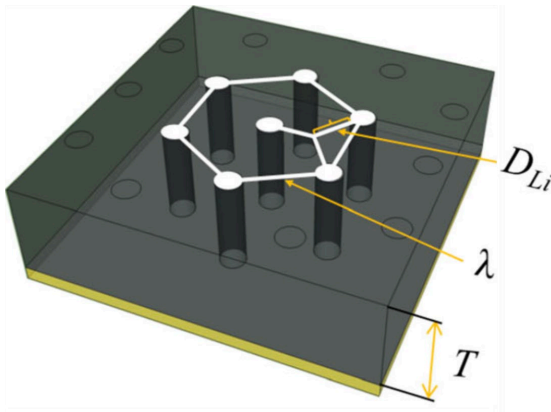
Operando characterization

PIs: Dasgupta, Karulkar

1. Operando microscopy and spectroscopy of Li plating
2. High-precision Coulometry
3. Rapid EIS

Technical Progress

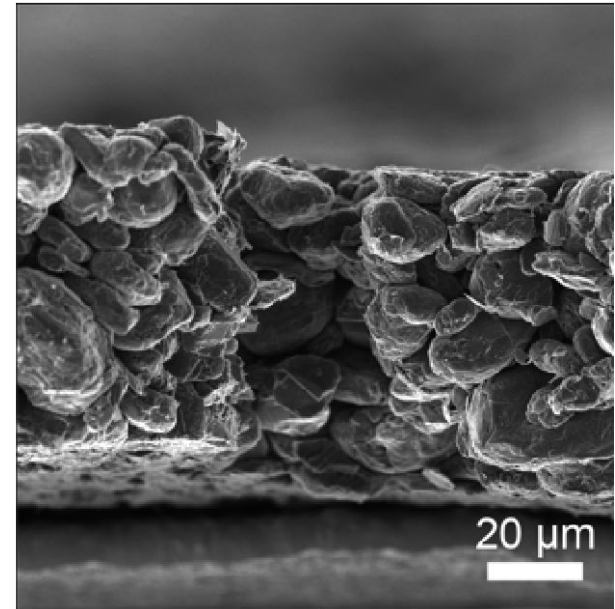
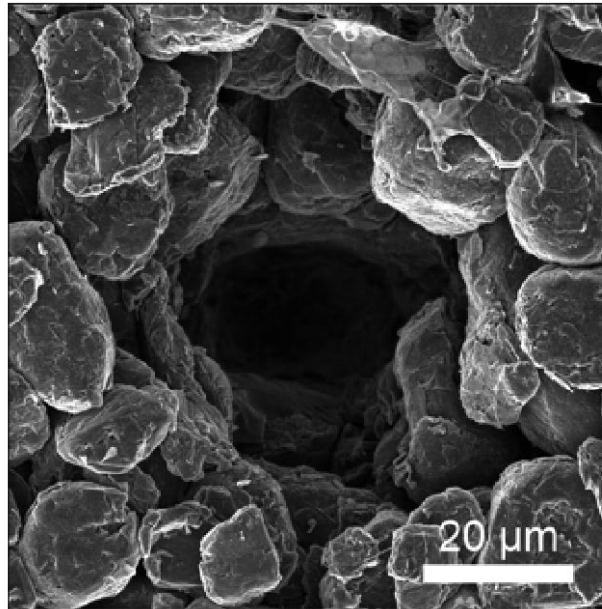
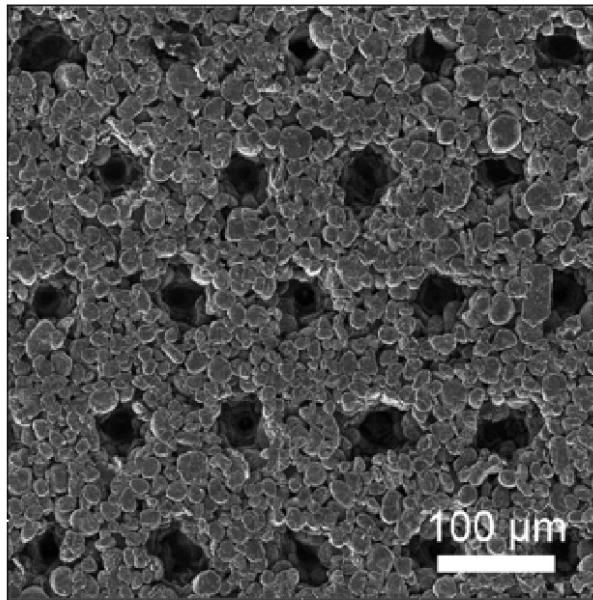
- Developed a laser manufacturing platform for high-throughput synthesis of highly ordered hierarchical (HOH) architectures with precise control of channel geometry



Technical Progress

- SEM/laser profilometry characterization on the HOH electrodes
- Parametric study on the effect of hole diameter and spacing

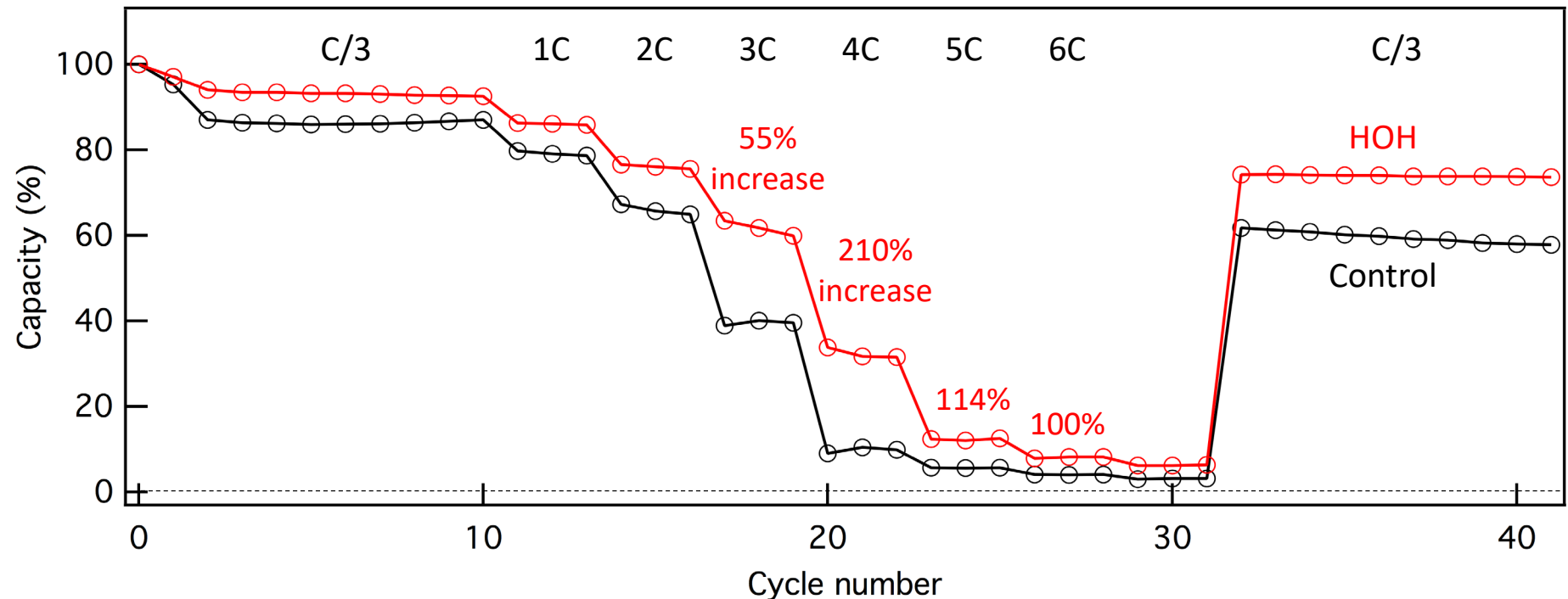
		Diameter		
		20 μm	35 μm	50 μm
Spacing	100 μm			
	150 μm			
	200 μm			



Technical Progress

HOH on graphite: >100% improvement in constant-current (CC) charge capacity retention in graphite electrodes using un-optimized HOH geometries

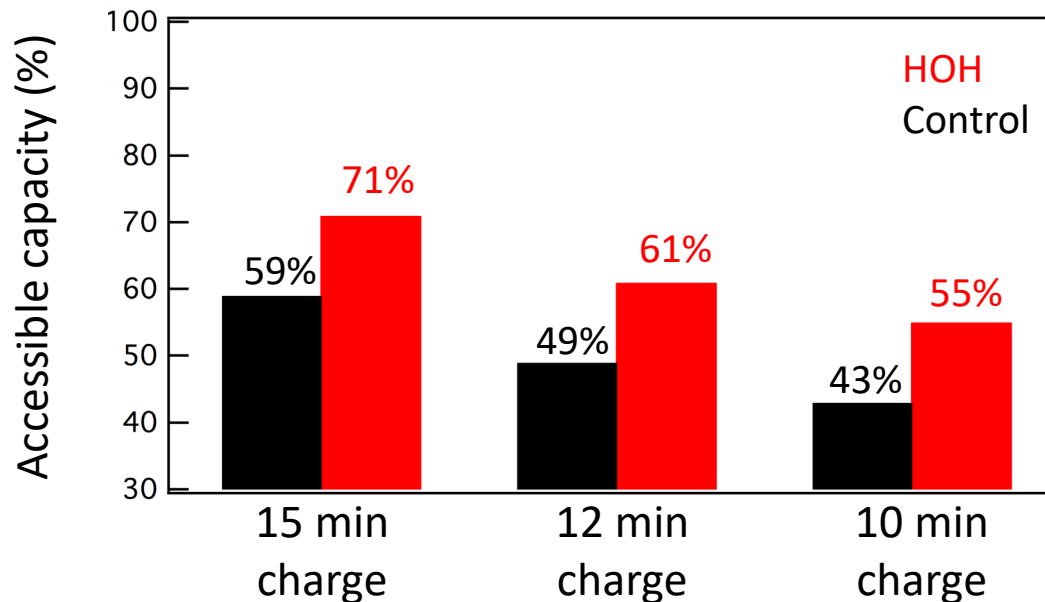
HOH on graphite (3 mAh/cm² areal loading)



Technical Progress

Demonstrated improved rate capability in graphite electrodes with un-optimized HOH geometries

Graphite anodes (3 mAh/cm² areal loading)



Technical Progress

- U-M battery lab: semi-automated, roll-to-roll processing facilities for electrode fabrication, electrode preparation, cell assembly, and battery testing



Electrode fabrication room

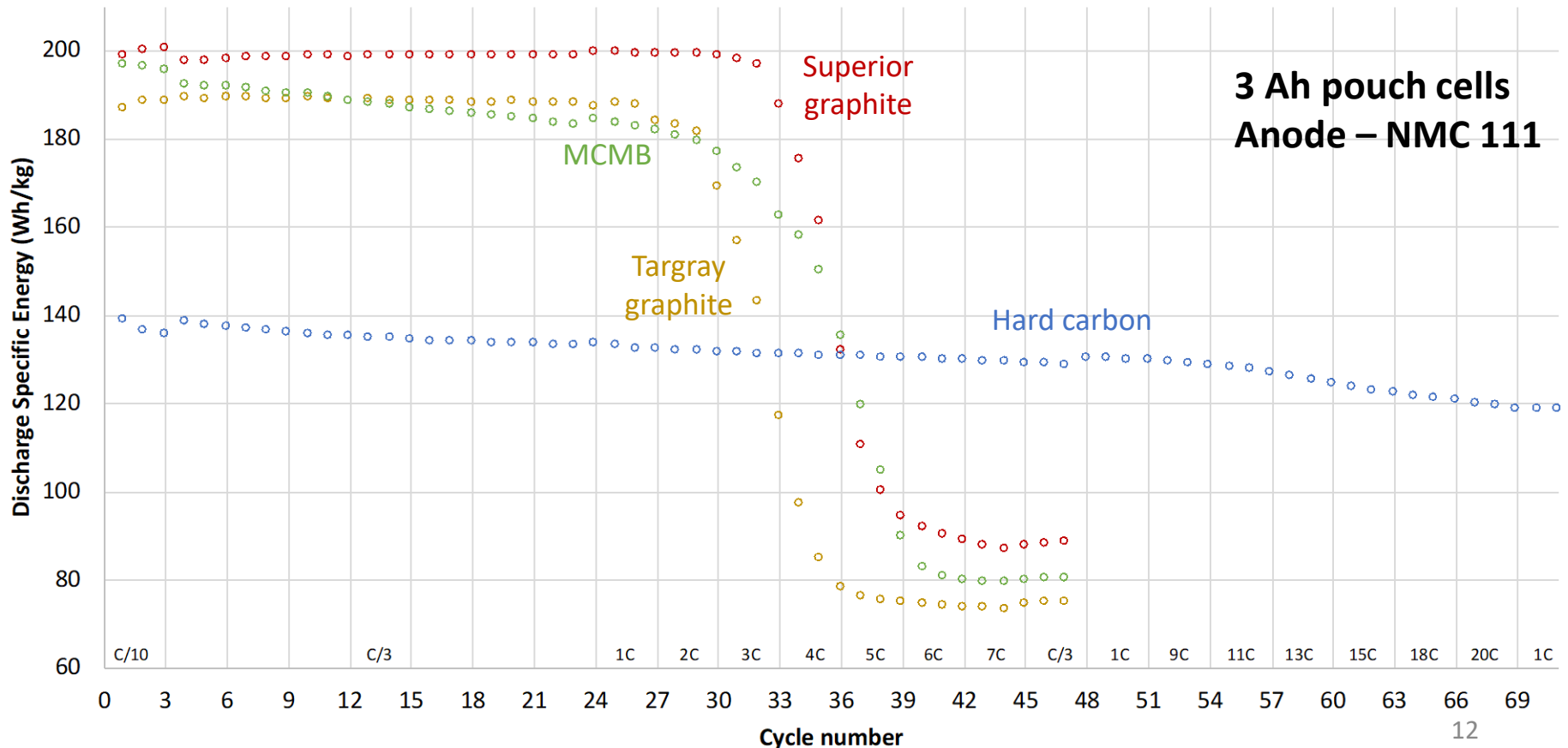


Dry room

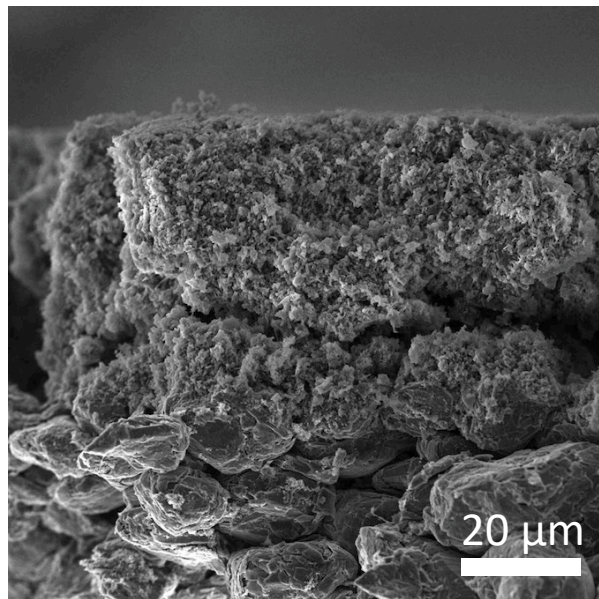
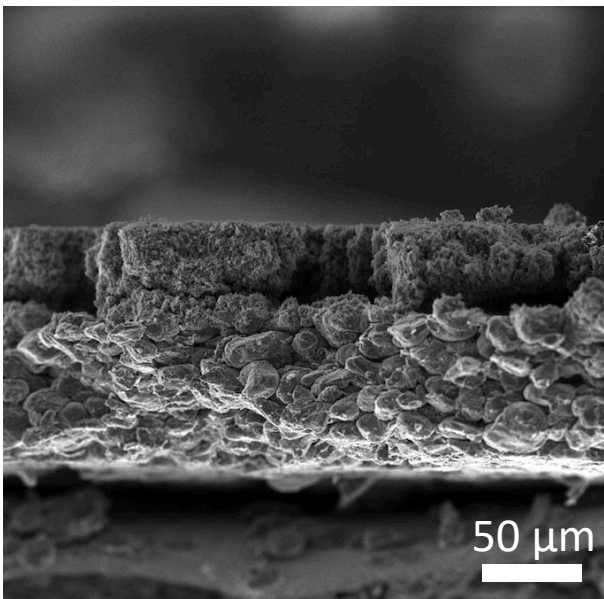
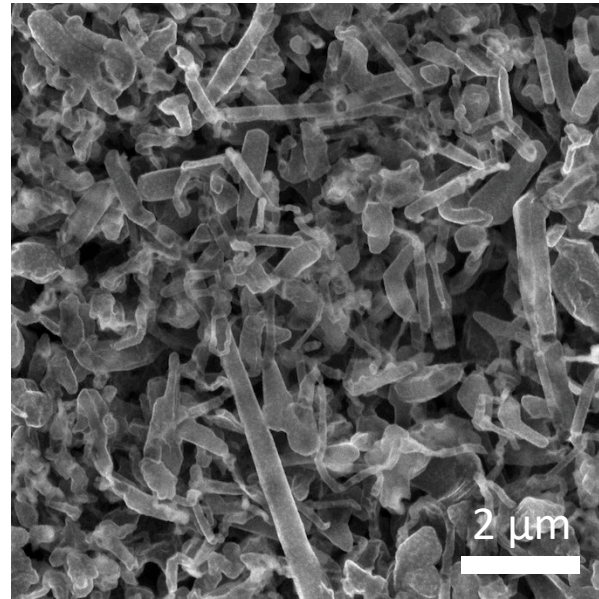
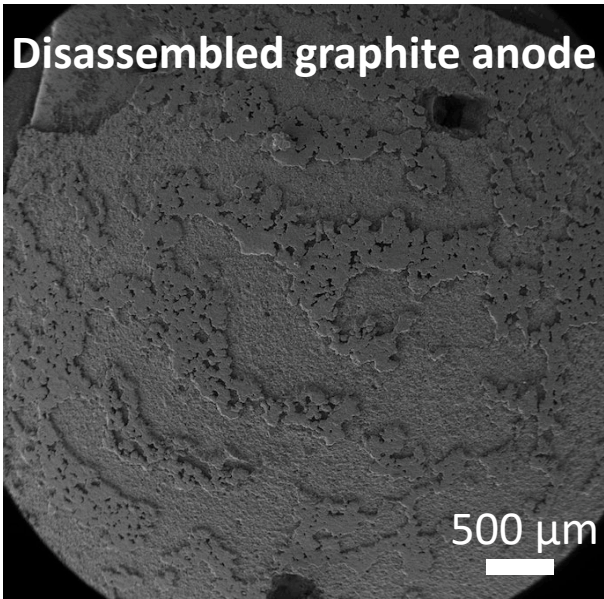


Technical Progress

- Down-selected anode materials from > 2Ah multilayer pouch cells
- Graphite cells show >180 Wh/kg, but Li plating at > 3C
- Hard carbon cells show good rate performance (up to 20C), but low initial Coulombic efficiency

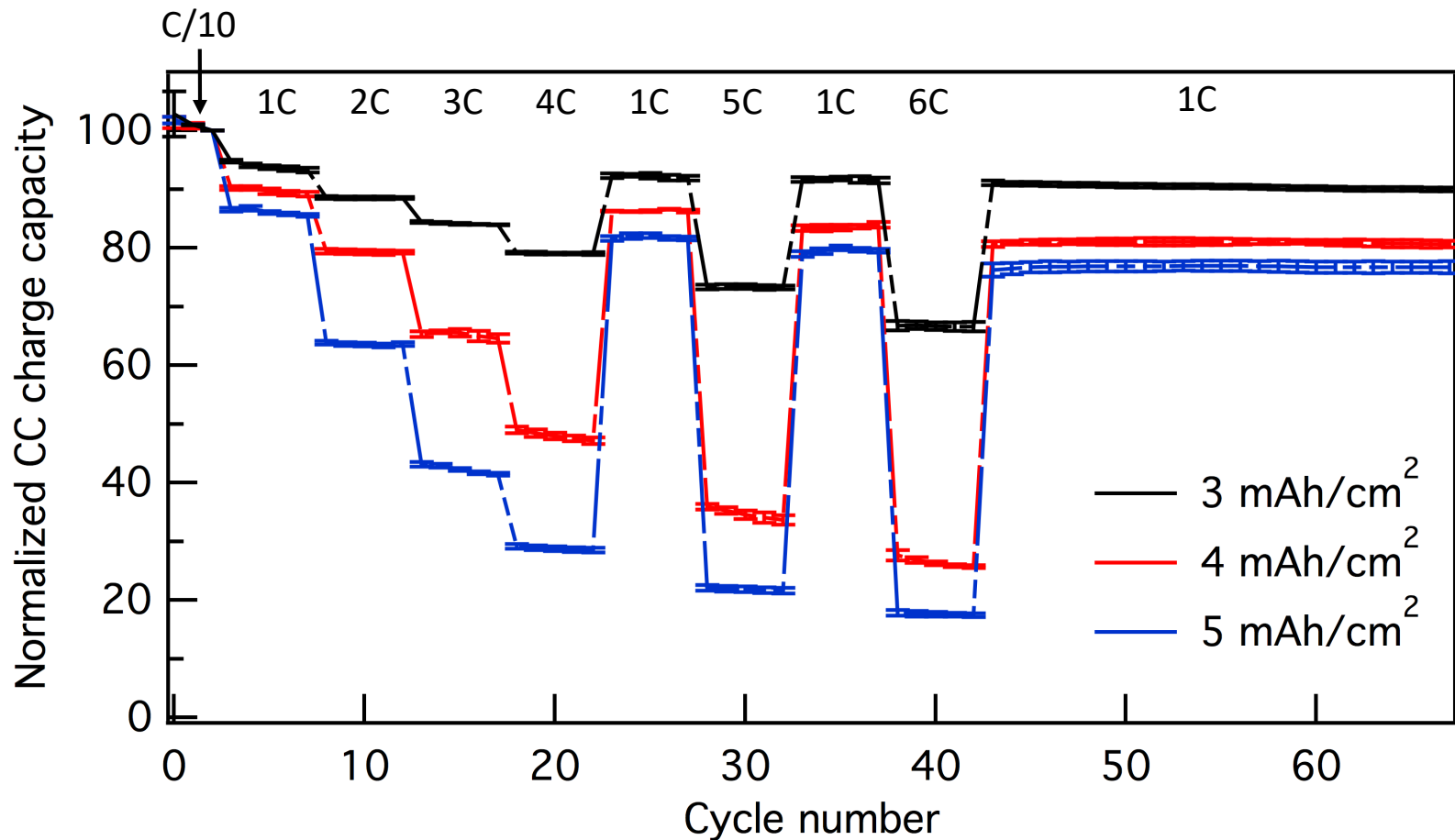


Technical Progress



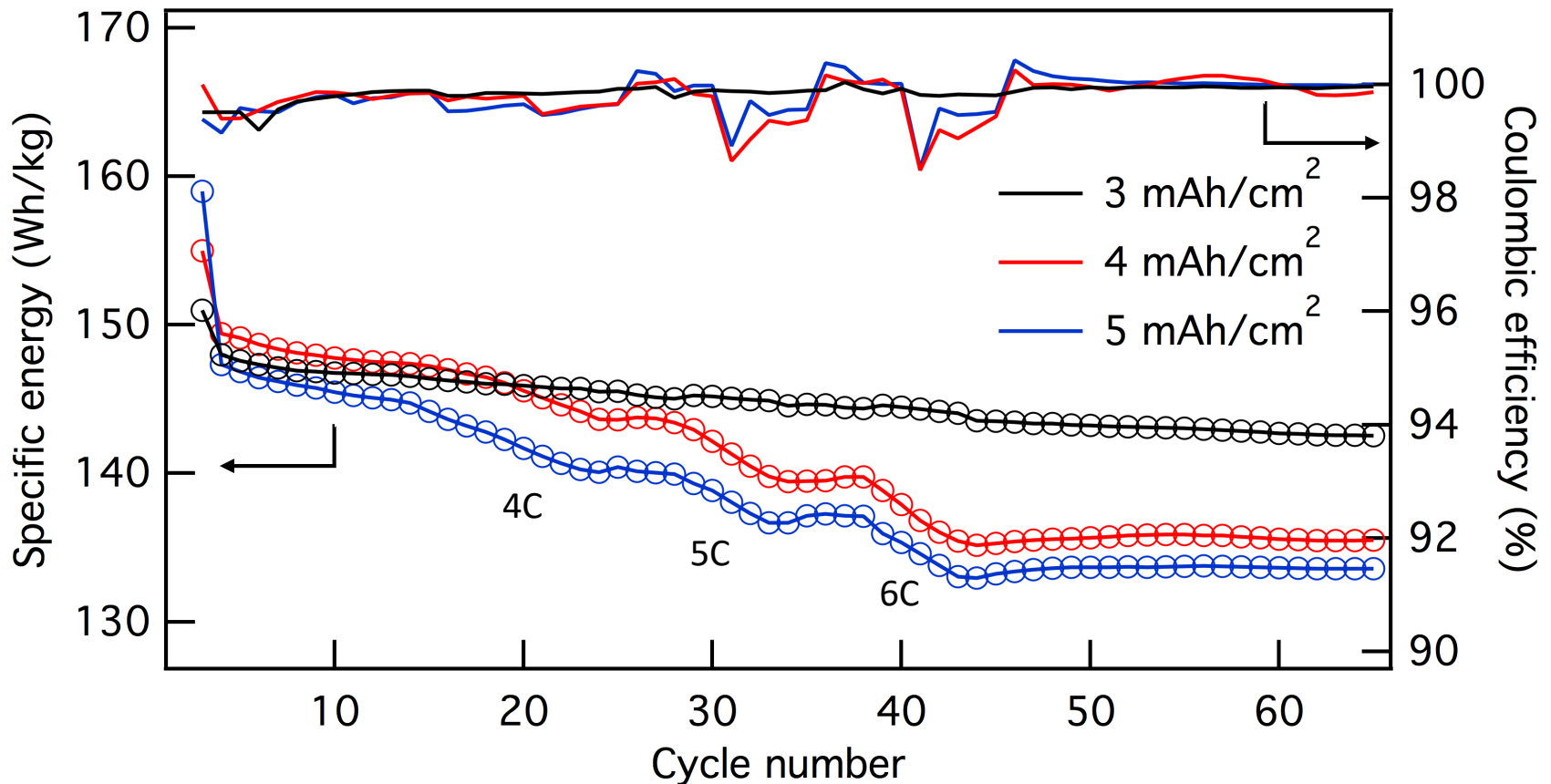
Technical Progress

Strong thickness-dependent effects were observed even with hard carbon anodes



Technical Progress

Li plating occurred in high-loading cells with hard carbon anodes
(with a corresponding dip in Coulombic efficiency)

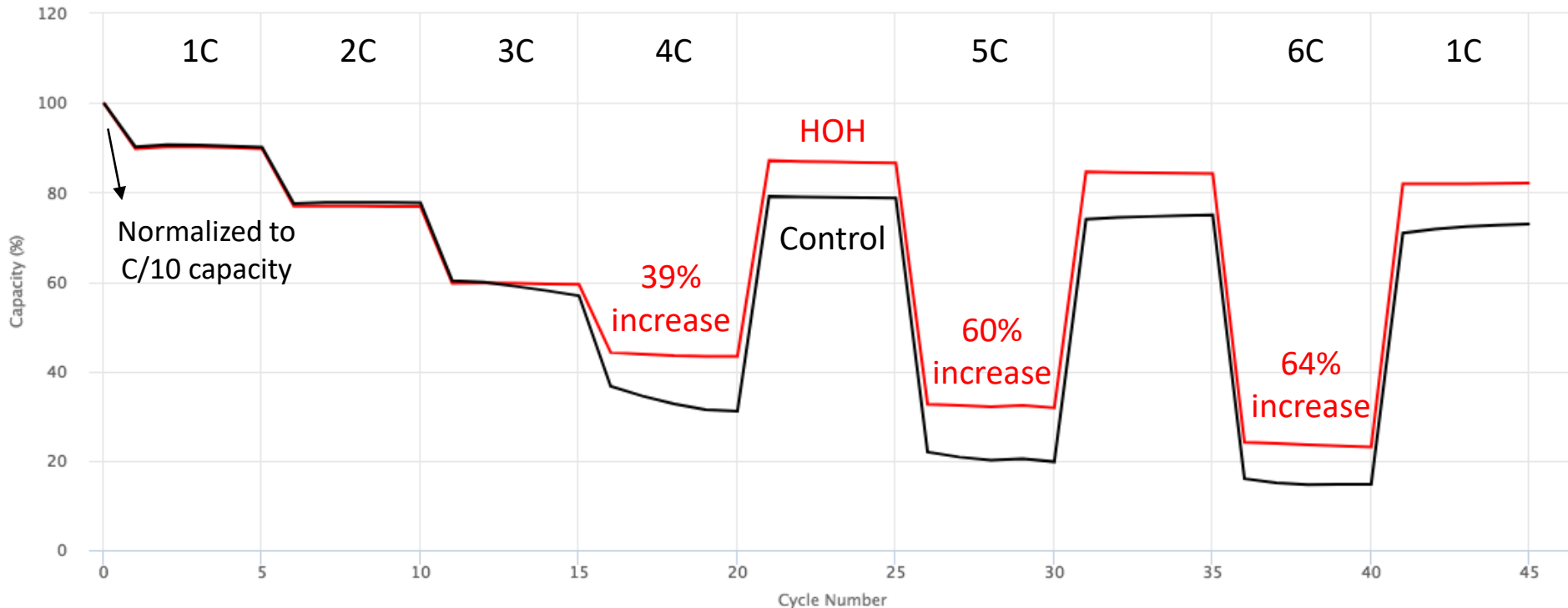


Technical Progress

Demonstrated improved rate capability in thick hard carbon cells with un-optimized HOH modification

HOH on hard carbon (5.45 mAh/cm² areal loading)

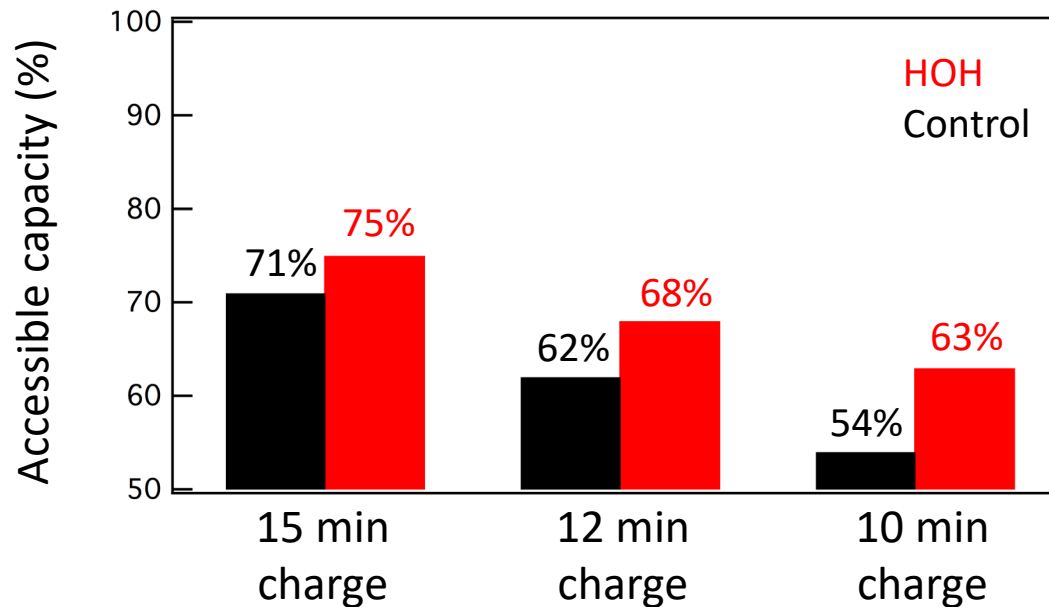
Normalized CC charge capacity



Technical Progress

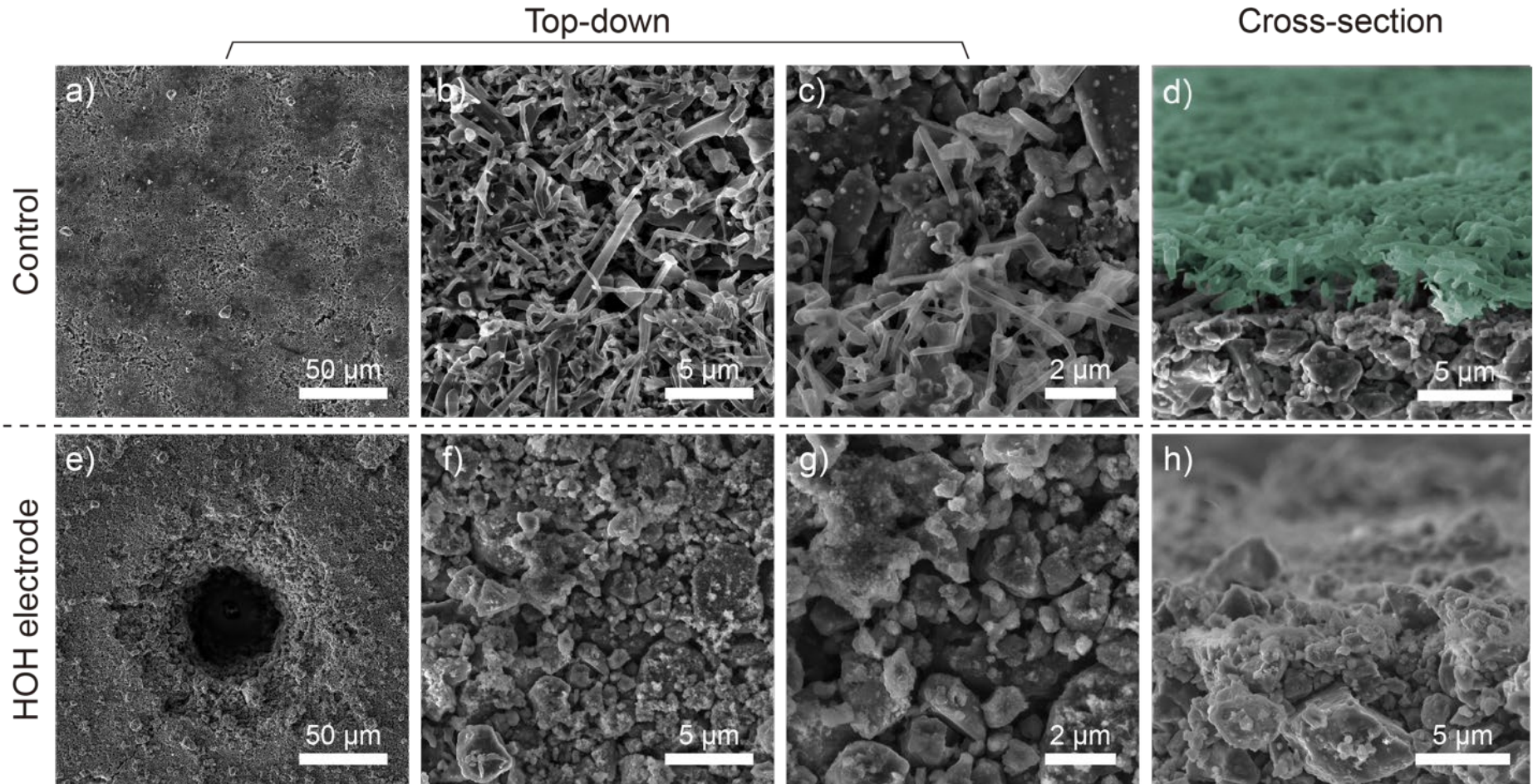
Demonstrated improved rate capability in thick hard carbon electrodes with un-optimized HOH modification

Hard carbon (5.45 mAh/cm² areal loading)



Technical Progress

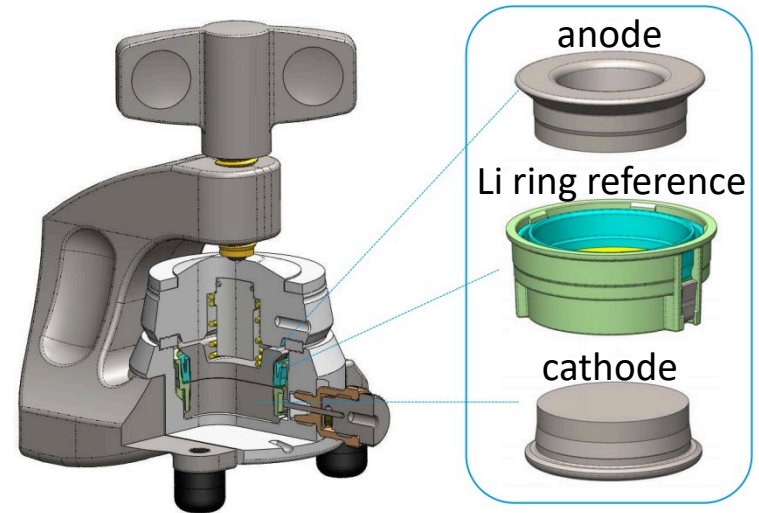
- Performed post-mortem SEM analysis after cycling
- Li plating occurred on control, but not on HOH sample



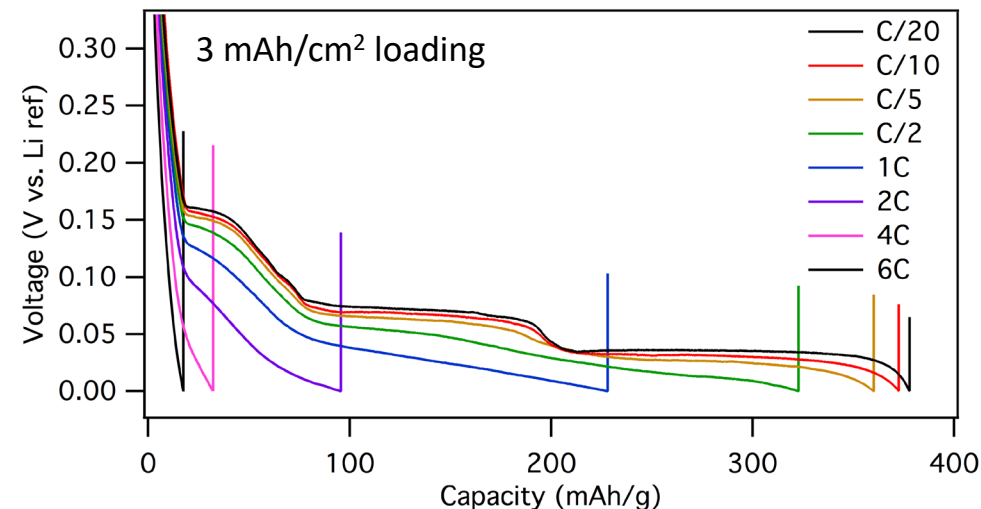
Technical Progress

- 3-electrode measurements to decouple anode/cathode voltage contribution
- Quantified the rate performance of different anode materials and HOH electrodes

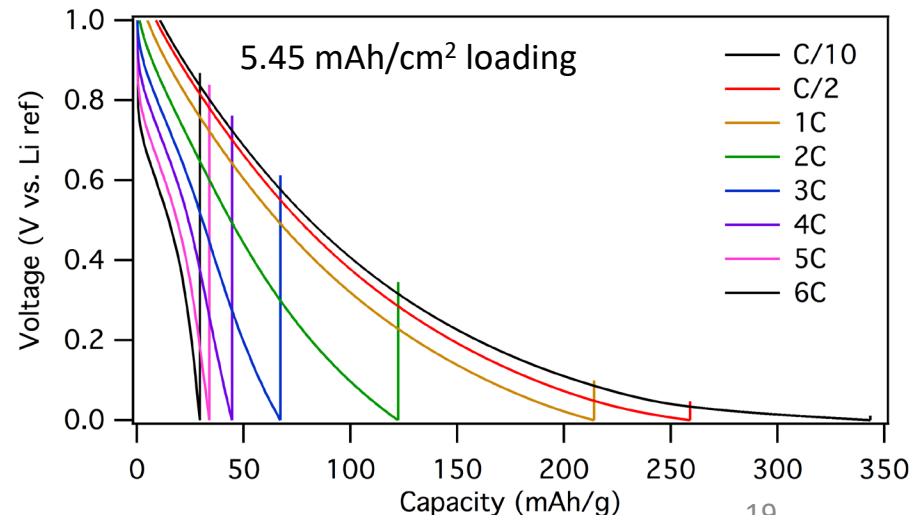
(EL-Cell®)



Graphite voltage

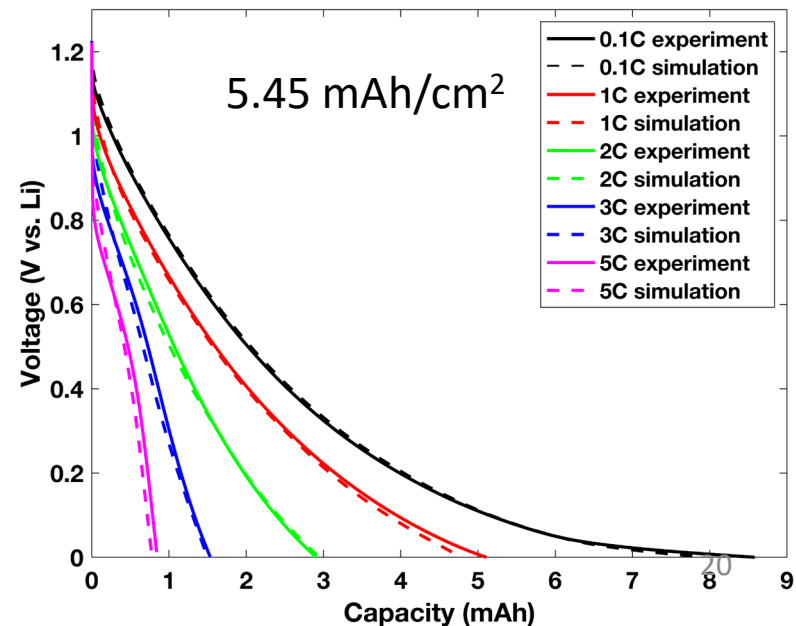
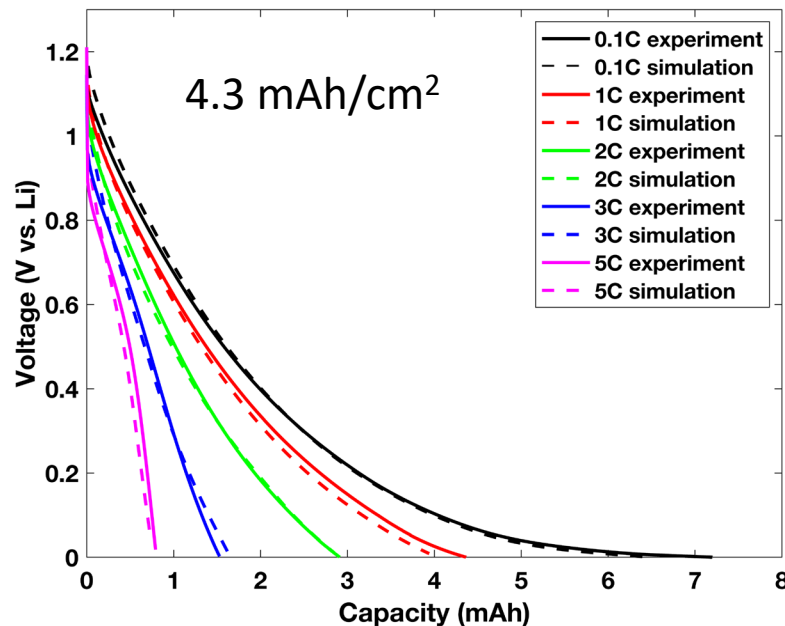
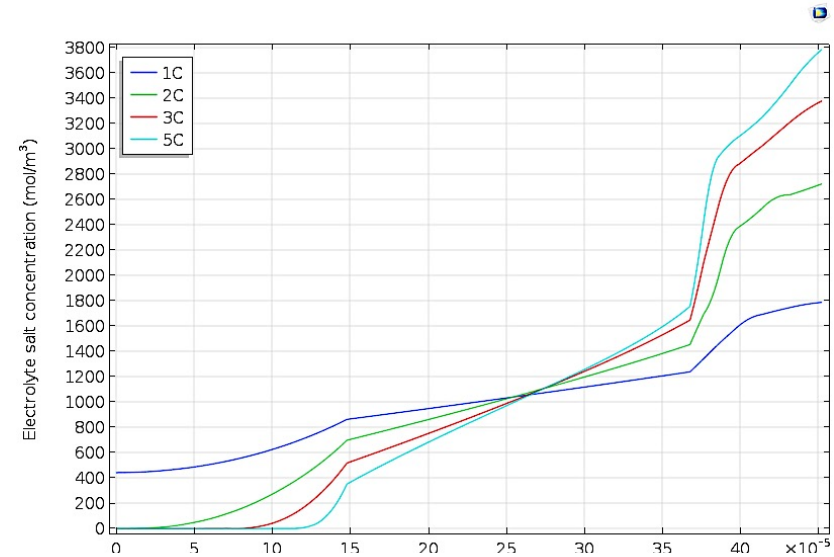


Hard carbon voltage



Technical Progress

- Developed an electrochemical dynamics simulation framework to model electrolyte concentration gradient and anode potential
- Good agreement with anode potential curves from 3-electrode measurements was achieved under two different electrode loadings



Responses to Previous Year Reviewers' comments

- This is the first year of this project

Collaboration & Coordination with Other Institutions

Sandia National Lab – Dr. Mohan Karulkar and Dr. Josh Lamb

- Leverage unique high precision Coulometry (HPC) and Rapid EIS capabilities in the Battery Abuse Lab (BattLab) to identify electrochemical signatures of plating during XFC conditions

Argonne National Lab – Andrew Jansen and Venkat Srinivasan

- Testing HOH modification of XFC electrode manufactured at CAMP facility

NREL – Kandler Smith

- Modeling of secondary pore geometry

SLAC – Dr. Mike Toney

- *Operando* synchrotron XRD of HOH electrodes during XFC

ETH Zürich – Prof. Vanessa Wood

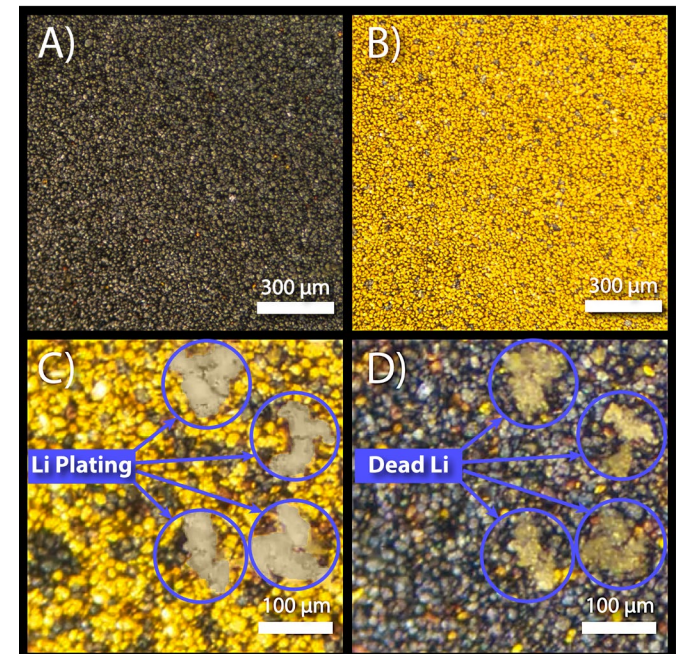
- X-ray tomography of HOH electrodes

Remaining Challenges and Barriers

- Improved fundamental understanding of and ability to detect Li plating under XFC conditions
- Interfacial modification of 3-D electrode architectures to enhance charge-transfer kinetics and suppress Li nucleation
- Incorporation of Li electrodeposition into modeling efforts

Proposed Future Research

- Manufacture >2Ah prototype batteries incorporating the HOH architecture, and demonstrate 200% improvement in capacity retention at 4C and 100% improvement of capacity retention at 6C over 100 cycles
- Demonstrate improved interfacial kinetics and homogeneity of lithium insertion across the electrode/electrolyte interface using ALD treatments
- Develop an improved fundamental understanding of Li plating on graphite using *operando* video microscopy and Raman spectroscopy



Any proposed future work is subject to change based on funding levels

Summary

- Designed and constructed high-power laser platform capable of rapid and scalable modification of pouch-cell-sized electrodes
- Demonstrated laser ablation of HOH geometries with tunable hole spacing and diameter, and characterized morphology
- Systematically investigated effect of HOH geometric parameters on rate capability and Li plating in graphite and hard carbon anodes, demonstrating significant improvement in rate capability and reduced Li plating
- Parameterized computational model informed by experimental results to simulate half-cell and full-cell charge/discharge curves and concentration grades
- Performed high-precision Coulometry and dV/dQ analysis on pouch cells at the Sandia National Laboratory BATLab